

# Formulation of disequilibrium for estimating the oceanic anthropogenic CO<sub>2</sub> over the Southern Ocean

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## 【Introduction】

The ocean is estimated to absorb approximately a quarter of the anthropogenic CO<sub>2</sub> released by human activity [Le Quere et al., 2015]. The ocean is thought to mitigate the effect of global warming. The Southern Ocean (SO) is expected to absorb 40% of the ocean uptake of anthropogenic CO<sub>2</sub> [Khatiwala et al., 2013]. Unfortunately, there are few observational data of carbonate materials (dissolved inorganic carbon (DIC), total alkalinity (TA), pH) for estimating the oceanic anthropogenic CO<sub>2</sub> due to severe weather conditions. It is difficult to grasp the detailed spatiotemporal dynamics of the oceanic anthropogenic CO<sub>2</sub> with high resolution.

On the other hand, in order to estimate the anthropogenic CO<sub>2</sub>, we must consider that two-step dissociation occurs when CO<sub>2</sub> dissolves in the ocean. It takes six months for CO<sub>2</sub> to reach the equilibrium in the surface mixed layer, which is about twenty times that of oxygen. Therefore, CO<sub>2</sub> is generally in a disequilibrium state at the air-sea interface [Sarmiento and Gruber, 2006]. To calculate the anthropogenic CO<sub>2</sub> in the seawater, the disequilibrium (DIC<sub>diseq</sub>) by the air-sea gas exchange is required. Additionally, we need to correct the effects of biological activities as remineralization and CaCO<sub>3</sub> dissolution (Eq. 1);

$$\text{DIC}_{\text{anth}} = \text{DIC}_{\text{obs}} - \text{DIC}_{\text{pi-sat}} - \text{DIC}_{\text{diseq}} - \text{DIC}_{\text{soft}} - \text{DIC}_{\text{carb}} \quad (\text{Eq. 1})$$

where the subscript, anth, obs, pi-sat, soft and carb mean the anthropogenic amount, the observational amount, the saturated amount in the pre-industrial era, the amount by remineralization of organic matter and the amount derived from CaCO<sub>3</sub> dissolution, respectively.

In previous studies, the chemical tracers must be used to estimate the DIC<sub>diseq</sub> [e.g., Gruber et al., 1996] while the measurement for the chemical tracers is awkward. Since the chemical tracers data are less than the basic hydrological data in the SO, it is difficult to estimate the anthropogenic CO<sub>2</sub> over the entire SO. In this study, we attempted to estimate the DIC<sub>diseq</sub> over the SO south of 30 °S without using the chemical tracers.

## 【Method and Data】

We assumed that CO<sub>2</sub> exchange at the air-sea interface is vertically constant within the surface mixed layer (MLD) of the ocean. In order to estimate the DIC<sub>diseq</sub>, we modified Eq. 1 to calculate the DIC<sub>MLD,diseq</sub> in the MLD (Eq. 2) [Li et al., 2019];

$$\text{DIC}_{\text{MLD,diseq}} = \text{DIC}_{\text{MLD,obs}} - \text{DIC}_{\text{MLD,sat}} - \text{DIC}_{\text{MLD,soft}} - \text{DIC}_{\text{MLD,carb}} \quad (\text{Eq. 2})$$

where the subscript, MLD means the value in the surface mixed layer. DIC<sub>MLD, sat</sub> is the current saturated DIC that can be calculated from the chemical equilibrium of seawater CO<sub>2</sub> and atmospheric pCO<sub>2</sub>. DIC<sub>MLD,soft</sub> and DIC<sub>MLD,carb</sub> can be obtained from the stoichiometric ratios of nitrogen, oxygen and carbon.

Using the GLODAP v2 data set such as temperature (T), salinity (S), dissolved oxygen (DO), apparent oxygen utilization (AOU), TA, and DIC in the MLD in the SO south of 30 °S, we calculated the DIC<sub>diseq</sub>. Based on the obtained DIC<sub>MLD,diseq</sub>, we attempted to obtain the parameterization for the DIC<sub>diseq</sub> with T, S and AOU.

## 【Results and Discussion】

We obtained the equation of DIC<sub>diseq</sub> as follow:

$$\text{DIC}_{\text{diseq}} (\mu\text{mol kg}^{-1}) = -203.5 + 0.8244 \cdot T + 5.547 \cdot S - 0.5170 \cdot \text{AOU} \quad (\text{Eq. 3})$$

$$(R^2 = 0.66, \text{RMSE} = 8.0 \mu\text{mol kg}^{-1}, n = 6,759)$$

Eq. 3 can allow us to obtain the DIC<sub>diseq</sub> from the surface to the bottom in the SO south of 30 °S. Furthermore, we will depict the detailed spatiotemporal changes in the anthropogenic CO<sub>2</sub> over the SO by applying Eq. 3 to the 466 Argo profiling floats during 2003-2019.